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(54) Process for the production of high molecular weight polyester.

(57) A process for the continuous production of high molecular weight polyester resin from a polyester resin granulate having a lower molecular weight, in which such granulate is subjected in series to a crystallization stage with stirring and with inert gas flow and therafter to a solid state polycondensation stage with inert gas flow, comprises the steps of recycling the inert gas flow to the polycondensation and crystallization stages, subjecting to an oxidation stage the inert gas flow leaving the crystallization stage, supplying directly the crystallization stage with a portion of the gas flow leaving the oxidation stage, purifying the remaining portion of the gas flow and supplying the polycondensation stage with such purified flow portion.

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DESCRIPTION

The present invention relates to a process for the continuous production of high molecular weight polyester resin from a polyester resin granulate having a lower molecular weight, in which the polyester granulate is subjected in series to a crystallization stage with stirring and with gas flow and thereafter to a solid state polycondensation stage with an inert gas flow.

This process is particularly suitable for the production of polyester resins, such as polyethylene terephthalate (PET) and polyethylene isophthalate, suitable for the production of bottles for carbonated beverages.

The main problem of the known processes consists in the

removal from the PET granulate of acetaldehyde and in the generation rate of acetaldehyde in the granulate, which, in the following step of tranformation of such granulate into the bottles can give some problems. Particularly in the production of bottles by stretch-blowing of preforms, it has been noted that high contents of acetaldehyde and particularly a high acetaldehyde generation rate in the granulate can lead to an increase of acetaldehyde contents in the preforms and in the walls of the bottles made from such preforms.

Moreover, in the crystallization stage the generation rate of acetaldehyde is particularly high.

Processes for the production of PET suitable for the production of bottles and containers, based on the solid state polycondensation, are described by U.S. patents No. 4,064,112 and No. 4.161,578. These processes differ from each other essentially in the different temperatures utilized in the crystallization and polycondensation stages. It has been noted that the acetaldehyde generation rate in the PET granulate subjected to the above mentioned known processes is still high, particularly in the crystallization stage, and this leads to poor properties of the bottles made from such granulate. It is important to emphasize that the above patents do not consider the problem of the generation rate of acetaldehyde during the overall process. Experiments made by the applicant have proved that with the process according to the above patents the generation rate of acetaldehyde is always higher than 0.3 ppm/min at 250°C.

The object of the present invention is to provide a process for the production of a polyester resin, particularly PET, having a high molecular weight, a content of residual acetaldehyde below 1 ppm and a very low generation rate of acetaldehyde during the overall process.

This object is achieved by virtue of the fact that the process comprises the steps of recycling continuously the gas flow in counter-current to the polycondensation and

crystallition stage; subjecting to an oxidation stage the inert gas flow leaving the crystallization stage, such inert gas including organic compounds produced in the crystallization and polycondensation stages; supplying directly without purification the crystallization stage with a portion of the gas flow leaving the oxidation stage; supplying a purification stage with the remaining portion of gas flow leaving the oxidation stage and supplying the policondensation stage with such remaining portion after purification.

By virtue of these characteristics, the generation rate of acetaldehyde of the resin is very low. Moreover, the flow rate of inert gas sent to the purification stage is reduced, with a saving on the apparatus.

Preferably, the portion of gas flow leaving the oxidation stage and supplying directly the crystallization stage, is comprised between 5 and 50% by weight of the total gas flow, more preferably between 5 and 20%.

Further advantages and features of the process according to the present invention will become clear from the detailed description which follows, purely by way of non-limiting example, with reference to practical examples regarding the process and to the appended drawings, in which:

Fig. 1 shows in a schematic way the lay-out of the process, and

Fig. 2 shows the analytical apparatus to determine the acetaldehyde generation rate.

With reference to the appended drawing, with 1 is indicated the granulate flow of polyester resin entering a crystallization stage 2 in which the granulate is subjected to stirring in order to avoid sticking. The apparatus of stage 2 can comprise, as an alternative, a stirred reactor, a screw reactor, a multi-tubular device or a fluidized bed reactor. The temperature in stage 2 is comprised between 170 and 220°C, preferably between 190 and 220°C. The granulate

flow leaving the crystallization stage 2 is fed, through a conveyor 3, to a fixed bed polycondensation stage 4 in which the temperature is maintained between 180°C and 245°C, preferably between 190 and 230°C. More preferably, the temperature in the polycondensation stage is maintained between 200 and 220°C and it is equal to the temperature of the crystallization stage. From the stage 4 a granulate flow 5 of polyester with a low content of acetaldehyde and having a low acetaldehyde generation rate is continuously extracted.

Nitrogen flows 6 and 7 are fed to the stages 4 and 2 in order to remove the volatile products which are formed in the polycondensation and crystallization stages, essentially ethylene glycol and acetaldehyde. The nitrogen flow leaving the stage 2, indicated with reference 8, is fed to an oxidation stage 9 having a catalytic fixed bed in order to oxidize the volatile organic compounds which are present in the nitrogen flow. The stage 9 can be constituted by a reactor of know type which utilizes air to oxidize the organic compounds in a temperature range between 250 and 400°C and which then removes the surplus of oxygen by catalytic hydrogenation to reach oxygen concentrations below 1 ppm. The volatile compounds which are present in the nitrogen flow 10 leaving the oxidation stage 9 have an ethylene glycol content below 1 ppm and an acetaldehyde content below 1 ppm. Moreover the nitrogen flow 10 has a content of CO_2 and water less than 5% by weight and less than 1% hydrogen by volume.

The nitrogen flow 10 is divided in two streams 11 and 12. The stream 12 is fed to a dryer 13 of commercial type i.e. utilizing silica gel or molecular sieves. The nitrogen flow 7 entering the crystallization stage 2 is the sum of stream 11 leaving the stage 9 and of stream 14 leaving the polycondensation stage 4.

The flow 7 entering the stage 2 has an acetaldehyde content and an ethylene glycol content both below 5 ppm,

preferably 2 ppm, and a CO_2 content higher than 0,1% by weight referred to the total gas flow. The concentration of oxygen in the flow 10 which leaves the oxidation stage is below 2 ppm, preferably 1 ppm.

In any stage of the process there is no addition of water or steam.

Crashed bottles of polyester can be advantageously utilized as starting material for the process. The final product obtained through the present process is particularly suitable for the production of carbonated beverages bottles.

In order to more clearly describe the process according to the present invention the following examples are given.

Example 1

The crystallization stage (stage 2 of the drawing) is supplied with 100 kg/h of PET pellets having an intrinsic viscosity 0.6 and an acetaldehyde content 140 ppm. In counter-current with the PET pellets are fed 80 kg/h of nitrogen coming from the combination of flows 11 and 14. The temperature of the stage 2 is maintained at 215°C and the residence time of the pellets is of 1.5 hours.

The pellets are then transferred to the polycondensation stage 4 to which is fed, in counter-current, the nitrogen flow 6 with a flow rate of 70 kg/h. The temperature during the polycondensation is maintained at 230°C and the residence time of the pellets in the stage 4 is 5.5 hours.

The produced PET has an intrinsic viscosity of 0.81, an acetaldehyde content of 0.3 ppm and the generation rate of acetaldehyde at 250°C is 0.13 ppm/min.

Example 2

The crystallization stage 2 is supplied with 100 kg/h of pellets of polyethylene terephthalate-isophthalate copolymer (CoPET), having a content of isophthalic groups of 5% by weight of polymer and an intrinsic viscosity of 0.58 and an acetaldehyde content of 110 ppm.

The treatment conditions as far as the inert gas flow and the residence time are concerned, are identical to those

of example 1, with the only difference that the temperature in the stages 2 and 4 is maintained at 218°C.

The produced copolymer has an intrinsic viscosity of 0.8 and an acetaldehyde content of 0.2 ppm. The generation rate of acetaldehyde at 250°C is 0.12 ppm/min.

Example 3

The crystallization stage 2 is supplied with 100 kg/h of not dried pellets of PET having an intrinsic viscosity of 0.6, an acetaldehyde content of 140 ppm. The recycled nitrogen flows are maintained equal to those of example 1 and 2.

The temperature during the crystallization is maintained at 170°C, with a residence time of 1.5 hours.

The temperature in the polycondensation stage is maintained at 215°C, with a residence time of 7.5 hours.

The produced PET has an intrinsic viscosity of 0.8 and an acetaldehyde content of 0.4 ppm. The generation rate of acetaldehyde at 250°C is 0.15 ppm/min.

Example 4

The crystallization stage 2 is supplied with 100 kg/h of crashed PET bottles having an intrinsic viscosity of 0.79 and an acetaldehyde content of 32 ppm. In counter-current with the crashed bottles, 80 kg/h of nitrogen coming from the combination of flows 11 and 14 are fed. The temperature of stage 2 is maintained at 230°C and the residence time is 1.5 hours.

The crashed bottles are then transferred to a polycondensation stage 4 to which the nitrogen flow 6 with a rate of 70 kg/h is fed in counter-current. The temperature during the polycondensation is maintained at 230°C, with a residence time of 3 hours.

The regradated crashed PET bottles, suitable for the production of new bioriented bottles, have an intrinsic viscosity of 0.8 and an acetaldehyde content of 0.1 ppm. The generation rate of acetaldehyde at 250°C is 0.13 ppm/min.

Hereinafter the methods followed to determine the

analytical data of the above examples are given.

The intrinsic viscosities have been determined on a solution of 0.5 g of polyester pellets in 100 ml of phenol/-tetrachloroethane solution with a ratio 1:1 at a temperature of 20°C.

The free acetaldehyde content has been determined with gas cromatographic methods previously described by DE-OS 28 34 162.

The thermal desorption technique has been used in our laboratory to determine the acetaldehyde generation rate.

We used the CARLO-ERBA-TDAS-5000 (thermal-desorption autosampler) in connection with CARLO-ERBA-GC. model HRGC 5300-Mega series and Mega series integrator model SP-4270.

With reference to Fig. 2, the tube 400 holding the PET-sample is inserted into the sampling position by the automatic loading mechanism and is heated to the desired temperature by the heater 130.

Carrier gas flowing through tube 400 transports the generated components through the switching value and low volume heated interface 600 into the split injector of the analytical GC 800. The components are cold trapped on a capillary column 900 at minus 62°C. We used Cryo unit to maintain the required temperature for the cold trapping. The capillary column was then heated by a selected temperature program till 230°C. The components were then detected by a FID-detector. The used instrumentations and conditions are the following:

- Instrumentations are all Carlo Erba
  - TDAS 5000, Thermal Desorption Autosamples and control unit
  - HRGC 5300 GC with flame ionization detector
  - Model SP-4270, Mega Series integrator
  - MFC 500 multifunction controller
  - Cryo 520-Control Module
  - Sub ambient temperature kit for Cryo-520
  - Messer Griesheim type Jupiter, 50 l Capacity, kit for

operations with liquid nitrogen.

Column:

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-	Column type	: capillary
-	Column material	: duran glass
-	Stationary phase	: PS 255
-	Dimensions	: 50 m x (0.5-0.55 mm I.D.)
-	Upper temperature limit	= +300°C

GC. Conditions:

-	Column temperature program	
	62 ---> 40°C	∞°C/min
	40°	2 min
	40° ---> 230°C	20°C/min
	Split flow	: 20ml/min
	Carrier gas	: He
	Gas pressure	: 1.1 Kg/cm²
	Detector	: FID , H_2 flow : 0.7 kg/h
		Air flow : 1 kg/h

BAD ORIGINAL

CLAIMS

1. Process for the continuous production of high molecular weight polyester resin from a polyester resin granulate having a lower molecular weight, in which such granulate is subjected in series to a crystallization stage with stirring and with inert gas flow and thereafter to a solid state polycondensation stage with inert gas flow, characterized in that it comprises the steps of:

a) recycling the inert gas flow continuously and in counter-current to the polycondensation and crystallization stages,

b) subjecting to an oxidation stage the inert gas flow leaving the crystallization stage, including volatile organic compounds produced in the crystallization and polycondensation stages,

c) supplying directly the crystallization stage with a portion of the gas flow leaving the oxidation stage, and

d) purifying the remaining portion of gas flow and supplying the polycondensation stage with such purified flow

portion.

2. Process according to Claim 1, characterized in that the portion (11) of inert gas flow leaving the oxidation stage and fed directly to the crystallization stage is comprised between 5 and 50% by weight of total inert gas flow (7).

3. Process according to Claim 1, characterized in that the total inert glas flow (7) fed to the crystallization stage has a temperature comprised between 170°C and 220°C.

4. Process according to Claim 1, characterized in that the portion of inert gas flow (6) fed to the polycondensation stage has a temperature comprised between 180°C and 245°C.

5. Process according to Claim 1, characterized in that the ratio between the flow rate by weight of granulate fed to crystallization stage and the flow rate by weight of inert gas flow (7) fed to the same stage is comprised between 0.5 and 2.

6. Process according to any of the preceding claims, characterized in that the polyester resin is polyethylene terephthalate.

7. Process according to any of the preceding claims 1-5, characterized in that such polyester resin is a copolymer of polyethylene terephthalate.

8. Process according to any of the preceding claims, characterized in that the temperature of crystallization stage is equal to the temperature of polycondensation stage and it is comprised between 200 and 220°C.

9. Process according to any of the preceding claims 1-6, characterized in that the polyester resin comprises crashed bottles of polyester.

10. Process according to any of the preceding claims, characterized in that such inert gas is nitrogen.

11. Process according to any of the preceeding claims, characterized in that the total inert gas flow (7) fed to the crystallization stage has a CO_2 content higher than 0.1% by weight referred to the total gas flow.

12. Process according to any of the preceding claims,

characterized in that no external water or steam is added to the recycled gas flow.

FIG. 1

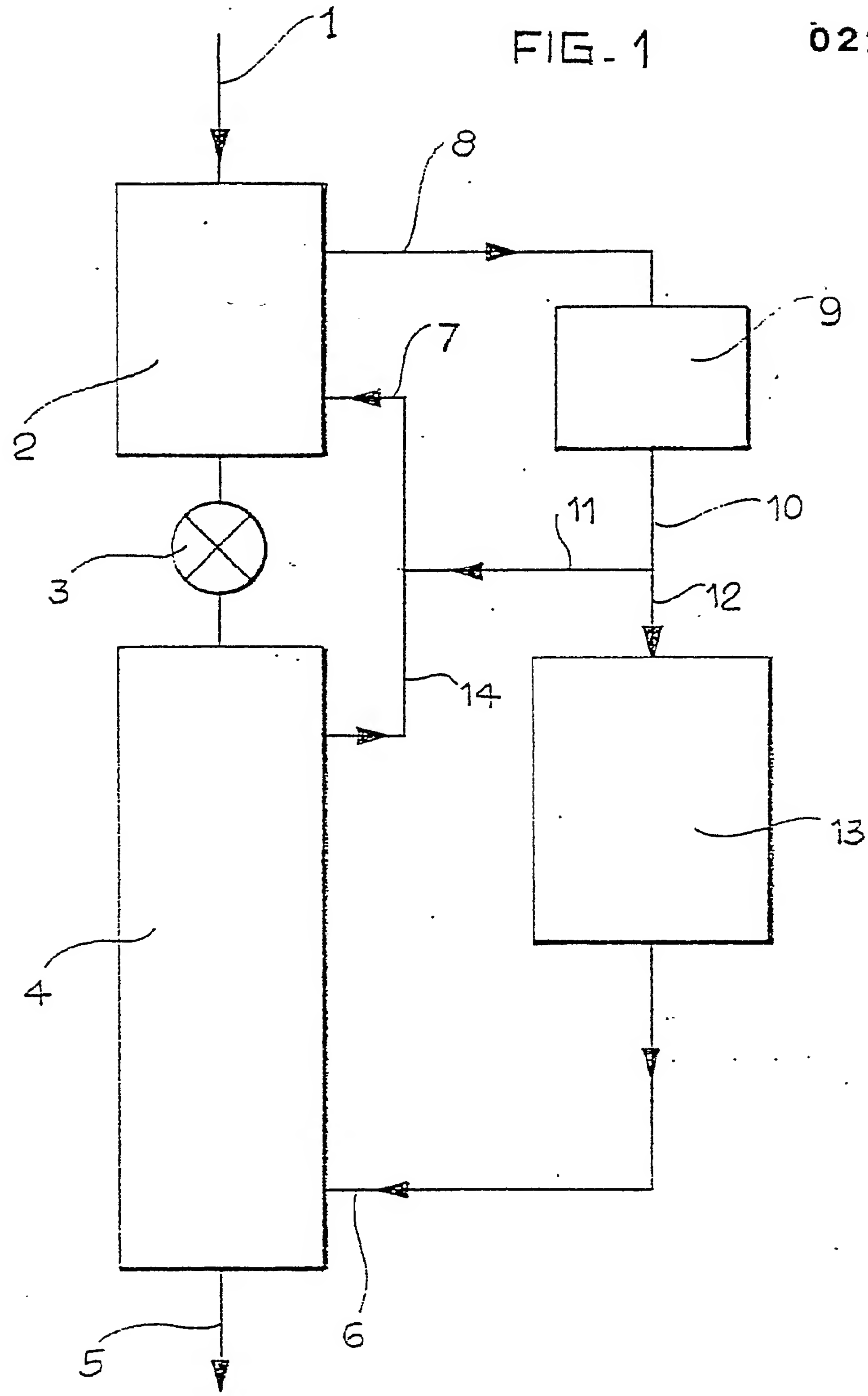

FIG_2